

ISOTOPIC AND ELEMENTAL COMPOSITION OF CHROMIUM, IRON, AND NICKEL IN TYPE I DEEP-SEA SPHERES: S. Xue<sup>1,2</sup>, C.-Y. Shih<sup>3</sup>, H. Wiesmann<sup>3</sup>, D.E. Brownlee<sup>4</sup>, G.S. Hall<sup>1</sup>, G.F. Herzog<sup>1</sup>, and L.E. Nyquist<sup>5</sup>; <sup>1</sup>Dept. Chemistry, Rutgers Univ., New Brunswick NJ 08903, USA, <sup>2</sup>Grad. School Oceanog., Narragansett Bay Campus, Univ. Rhode Island, Narragansett RI 02882-1197, USA, <sup>3</sup>Mail Code C23, Lockheed-Martin, 2400 NASA Road 1, Houston TX 77258, USA, <sup>4</sup>Dept. Astronomy, Univ. Washington, Seattle WA 98105, USA, <sup>5</sup>NASA Johnson Space Center, Houston TX 77058, USA.

**Summary** - We report analyses of Cr, Fe, and Ni in type I deep-sea spheres with masses ranging from 43 to 246  $\mu\text{g}$ . The isotopic compositions of Cr and of Fe were measured by TIMS; the elemental concentrations of Cr, Fe, and Ni and the isotopic compositions of Ni were measured by ICP-MS. In most spheres evaporation has led to significant and similar *average* degrees of mass-dependent fractionation,  $\Phi$ , for all three elements. The average value,  $\langle\Phi\rangle \sim 15\text{ }\text{‰}/\text{AMU}$ , corresponds to mass losses of 80-85% assuming open-system evaporation of the atoms. We find that 1)  $\Phi_{\text{Ni}} \propto (\Phi_{\text{Fe}})^n$ ,  $n \sim 3$ , perhaps because Ni evaporates more slowly than Fe but faster than FeO; and 2)  $\Phi_{\text{Cr}} \sim \Phi_{\text{Fe}}$  for all  $\Phi_{\text{Fe}}$ .

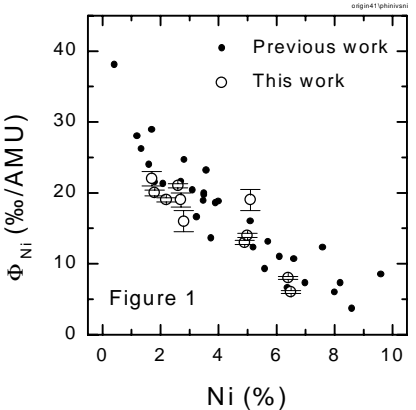
**Background** - Type I deep-sea spheres consist mainly of O, Fe, and Ni, which may occur as magnetite, wüstite, hematite, and/or metal, and of other elements in smaller concentrations. Kyte [1] pointed out that Cr/Fe ratios are diagnostic for certain kinds of meteoritic metal and therefore could help in identifying parent materials for the type I spheres. Of late it has become clear that heating of type I spheres during atmospheric entry caused large evaporative losses and, along with them, mass-dependent fractionation of the isotopic abundances of O, Fe, and Ni [2-6]. To the extent that such losses differ for each element, they must be known before the composition of a sphere as received can be related to that of the parent material. Similarly, the losses must be known in order to relate the observed masses to the pre-atmospheric masses. Under certain conditions the extent of isotopic fractionation of an element can furnish a measure of the degree of loss. In a study of eight type I spheres Davis and Brownlee [4] found that  $\Phi_{\text{Fe}}$  does not equal  $\Phi_{\text{Ni}}$ . Nyquist et al. [7], in oral presentation, reported isotopic data for Cr, Fe, and/or Ni in four spheres. We expand on this earlier work in an effort to learn more about the initial sizes and elemental ratios of type I spheres.

**Experimental methods and results** - We used the methods of [7] to measure the concentrations and isotopic ratios of Cr, Fe, and Ni in type I spheres. From the isotopic ratios we obtained  $\Phi$  by calculating  $\delta$ -values, plotting them vs. mass, and reading the slope. Table 1 compares averages of the new elemental concentrations and those of [7] (“This work”) with literature values. Most of the Fe contents fall in the range between 60-75% by mass; Cr and Ni contents vary by well over a factor of ten just as in [1] and [8]. Among our 13 spheres, 2 contained very little Ni ( $<0.1\%$ ); in ref. [8], 16/57 spheres have very low Ni contents. Kyte [1, Table 1], reported Ni contents below a

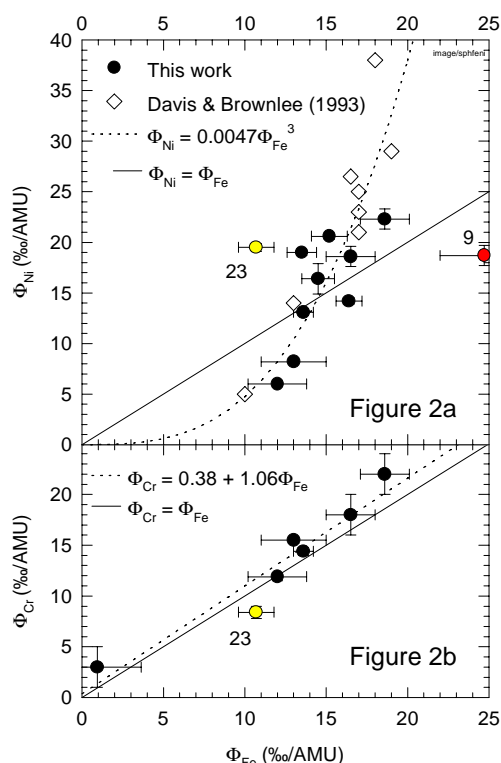
detection limit of  $\sim 0.5$  for 2 of 15 spheres. In light of [9], we hesitate to write off these low-Ni objects as terrestrial but treat them separately. As for Cr, the range 0.16 to 4.03  $\text{‰}$  includes all samples except the outlier KK1-23 (16.4 $\text{‰}$  Cr).

In agreement with previous work for whole spheres [6], we find that  $\Phi_{\text{Ni}}$  correlates inversely with Ni (Figure 1). Similar but weaker trends can be seen for  $\Phi_{\text{Fe}}$  and  $\Phi_{\text{Cr}}$  vs. Ni content if one outlier (KK1-9) and one sphere with unusually high Cr (KK1-23) are excluded.

Although the average degree of mass-dependent fractionation ( $\text{‰}/\text{AMU}$ ) is similar for Cr ( $15.0 \pm 4.7$ ), Fe ( $15.3 \pm 5.6$ ), and Ni ( $16.1 \pm 5.2$ ), the detailed relations differ. Figure 2a confirms



## Cr, Fe, AND Ni IN DEEP-SEA SPHERES: Xue et al.



the observation of [4] that  $\Phi_{\text{Ni}}$  at first increases more slowly and then more rapidly than  $\Phi_{\text{Fe}}$ . Figure 2b shows that  $\Phi_{\text{Cr}}$  increases at about the same rate as  $\Phi_{\text{Fe}}$ ; the data are consistent with a one-to-one linear relationship.

**Discussion** - The trends in Figure 2 can be understood if the evaporation rate of Fe initially exceeds that of Ni and then slows as metallic iron forms a less volatile oxide. The oxygen isotopic data suggest that evaporation of iron oxide remains appreciable, however. Average values of oxygen fractionation,  $\Phi_{\text{O}}$ , measured for comparable or greater numbers of spheres of various sizes [2] and recalculated relative to air assuming no kinetic isotope effect during oxidation of iron, are as follows:  $\Phi_{\text{O-air}} = 12.4$  ( $\sim 400\mu\text{m}$ ); 9.6 (240-340  $\mu\text{m}$ ); and 8.4 (100-150  $\mu\text{m}$ ). If we model the evaporation of Cr, Fe, and Ni as an open system distillation of the monoatoms and of oxygen as a species with a fractionation factor for  $^{17}\text{O}/^{16}\text{O}$  of 1.0110 [10], then the average values of  $\Phi$ ,  $\langle\Phi\rangle$ , correspond to losses of 80-85% for the transition metals but only about 60% for oxygen ( $\langle\Phi_{\text{O}}\rangle=9.6$ ). Use of the Rayleigh equation shows that the accompanying loss of 60% of the oxidized iron could

account for  $\sim 8$  of the 15 %/AMU of  $\langle\Phi_{\text{Fe}}\rangle$ . The other 7 %/AMU of  $\langle\Phi_{\text{Fe}}\rangle$  may result from early and more rapid evaporation of Fe as metal. We note that the fit of Figure 2a turns upward ( $d\Phi_{\text{Ni}} / d\Phi_{\text{Fe}} \geq 1$ ) at  $\Phi_{\text{Fe}} \sim 8$  %/AMU.

The similar values of  $\Phi_{\text{Cr}}$  and  $\Phi_{\text{Fe}}$  imply that measured Cr/Fe ratios, which average  $\sim 0.002$ , changed little during sphere formation; evidently Cr behaved chemically much as did Fe. Figure 3 compares Cr/Fe ratios for type I spheres (bars) [1,7,8] with average bulk values for selected meteorite groups. (Meteorite group names are plotted at the appropriate Cr/Fe ratios, but arbitrary heights). If Type I spheres form from chondritic matter, then the process fractionates Fe and Cr. The Cr/Fe ratios in kamacite from C-chondrites,  $\sim 0.001$ - $0.006$  [11] (not plotted), are a fair match to the observations.

The isotopic data indicate average evaporative losses of 80-85% for Cr, Fe, and Ni. Observed type I sphere masses must therefore be increased by at least a factor of 5 to obtain initial masses, and by more if ablative losses occurred (see also [12]). The decrease in diameter due to evaporation is counterbalanced by the formation of lower density oxide from higher density metal.

**References** - [1] Kyte F.T. (1983) *Ph.D. Thesis* University of California, Los Angeles, CA. [2] Clayton R.N. et al. (1986) *Earth Planet. Sci. Lett.* **79**, 235-240. [3] Davis A.M. et al. (1991) *Lunar Planet. Sci.* **XXII**, 281-282. [4] Davis A.M. and Brownlee D.E. (1993) *Lunar Planet. Sci.* **XXIV**, 373-374. [5] Herzog G.F. et al. (1994) *Geochim. Cosmochim. Acta* **58**, 5319-5323. [6] Xue S. et al. (1995) *Geochim. Cosmochim. Acta* **59**, 4975-4981. [7] Nyquist L.E. et al. (1995) *Meteoritics* **30**, 558-559. [8] Czajkowski J. (1987) Ph.D. Dissertation, University of California, San Diego. [9] Nishiizumi K. et al. (1995) *Meteoritics* **30**, 728-732. [10] Wang J. et al. (1994) *Lunar Planet. Sci.* **XXV**, 1459-1460. [11] Rambaldi E.R. and Wasson J.T. (1981) *Geochim. Cosmochim. Acta* **45**, 1001-1015. [12] Yada T. et al. (1996) *Proc. Natl. Inst. Polar Research Symp. Antarct. Meteorites* **9**, 218-236.

